Calibration of Intramolecular Radical Cation Probes Based on Arylalkene Cycloadditions[1]

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Abstract: The radical cations of three probe molecules (**1**−**3**) that undergo intramolecular cyclobutanation or Diels−Alder reactions have been generated by both photoionization and photosensitized electron transfer. In each case, flash photolysis experiments indicate formation of an initial radical cation with λ_{max} at ∼600 nm that is localized on the arylalkene moiety. The radical cations of **1** and **3** have decay rate constants of 1.2×10^9 and 3.0×10^8 s^{-1} and can only be observed by picosecond spectroscopy. These cyclization rate constants agree reasonably well with previous estimates based on product and Stern−Volmer quenching studies using a triarylaminium salt as the electron transfer catalyst. The transient experiments are consistent with cyclization of **1**$^{•+}$ to give a cyclobutane radical cation that has a lifetime of ∼100 ns and decays by either reduction to cyclobutane or rearrangement to a hexatriene radical cation, λ_{max} at 500 nm (**10**), but does not revert to **1**$^{•+}$. Consistent with this, product studies under photosensitized electron transfer conditions demonstrate that both substituted cyclobutane (**5**) and dihydronaphthalene (**8**) products are formed, with the relative amounts depending on the concentration of **1**. Radical cation **2**$^{•+}$ is relatively long-lived with an apparent decay rate constant of 3×10^6 s^{-1}; transient studies again provide evidence for rearrangement to a hexatriene radical cation. The observed decay rate is much lower than previous estimates and may indicate that the initial cyclobutane radical cation undergoes rapid cleavage (as observed for the *all-trans*-1,2-dianisyl-3,4-dimethylcyclobutane radical cation) in competition with rearrangement. The results illustrate some of the limitations that may be encountered in the development and calibration of intramolecular radical cation probes based on arylalkene cycloaddition chemistry.

Introduction

There has been considerable recent interest in developing molecules that act as mechanistic probes for the presence of radical and ionic intermediates in complex biological transformations. Much of this work has focused on radical probes and in particular cyclization reactions such as the 5-hexenyl to cyclopentylmethyl radical rearrangement.[2] The original work has now been extended to provide a wide range of radical clocks and probes that undergo characteristic unimolecular reactions with rate constants ranging from the millisecond to picosecond time scales.[3] These systems have been used both as probes for the intermediacy of radicals in biological mechanisms and as clocks to obtain kinetic information for competing intermolecular reactions by measuring relative product yields in place of direct time-resolved techniques.

By contrast to the wide range of radical probes that are now available, there have been relatively few investigations of intramolecular radical ion reactions that are suitable for use as mechanistic probes.[4−9] Most of the available systems involve bond cleavage reactions, as for example in the carbon−carbon

bond cleavages of appropriately-substituted arylethane radical anions and cations.[5,6] Recently, one of us has reported pioneering work on the development of probes based on intramolecular cycloaddition chemistry of arylalkene radical cations.[10,11] Intermolecular cycloaddition reactions of arylalkene radical cations leading to either cyclobutane or Diels−Alder adducts have been extensively studied and thus provide useful analogs for developing intramolecular radical cation probes.[9,12−22] The probe molecules, **1**−**3** in Scheme 1, are based on the

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[⊗] Abstract published in *Advance ACS Abstracts,* October 1, 1997.
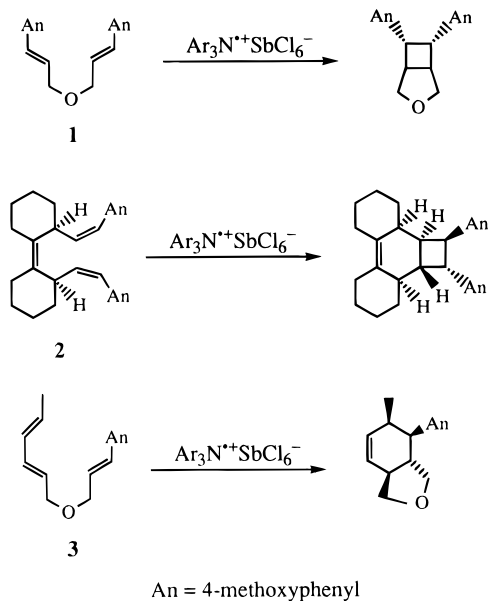(1) Issued as NRCC-40838.
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Scheme 1

An = 4-methoxyphenyl

Figure 1. Transient absorption spectra measured immediately after 308-nm laser irradiation of *trans*-anethole (●) and *cis*-anethole (○) (top) and *trans*-3-methoxy-1-(4-methoxyphenyl)-1-propene (bottom) in air-saturated acetonitrile.
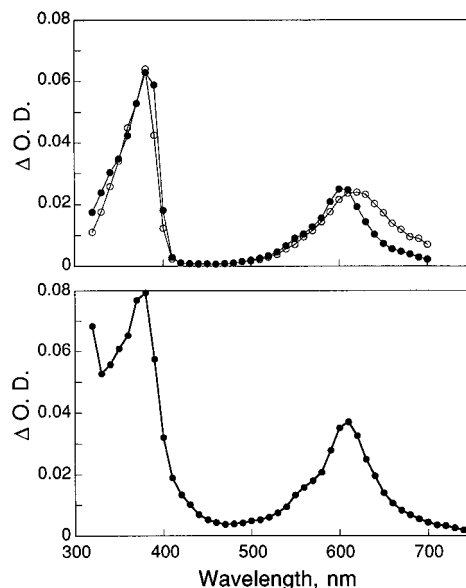
intramolecular cyclobutanation and Diels−Alder cycloaddition of anethole radical cations tethered to either a second arylalkene or a conjugated diene.[23] The original work demonstrated that the generation of the radical cations of probes **1**−**3** using a triarylaminium salt as the electron transfer catalyst resulted in efficient cyclization to give the expected cyclobutane and Diels−Alder adducts (Scheme 1). Rate constants for cyclization ranging from 3×10^7 to $>3 \times 10^9$ s^{-1} were determined indirectly by competitive kinetics methods, suggesting that these systems are well-suited as probes for short-lived radical cations. Probes **1**−**3** have been used to test for the importance of electron transfer reactions in metalloporphyrin-catalyzed epoxidations of alkenes and in tetracyanoethylene cycloaddition reactions.[11,24] In the present work, we have used picosecond and nanosecond laser flash photolysis to generate the arylalkene radical cations of **1**−**3** and to obtain absolute kinetic data for their rapid intramolecular cyclization reactions.[25] The results also provide insight into the mechanism for the radical cation cyclization reactions under photoinduced electron transfer conditions and illustrate some of the limitations to the use of radical cation probes based on cycloaddition chemistry.

Results

Nanosecond Flash Photolysis of Arylalkene Models. Spectroscopic and kinetic data for radical cations derived from several model arylalkenes were obtained for comparison with the results for the three intramolecular probes. As described previously, arylalkene radical cations can be generated readily using laser flash photolysis with a variety of techniques, including photoionization, chloranil sensitization, and 9,10-

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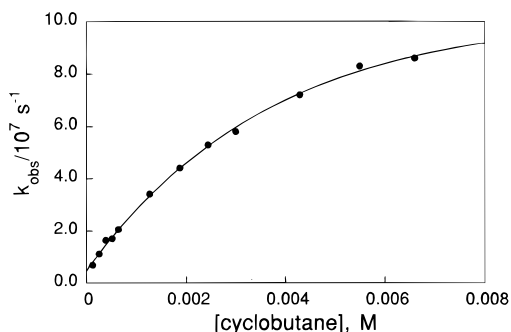
(24) Kim, T.; Sarker, H.; Bauld, N. L. *J. Chem. Soc., Perkin Trans. 2* **1995**, 577−580.

(25) Preliminary results have been reported.[9,24]

dicyanoanthracene sensitization using biphenyl as a cosensitizer.[9,26−28] The absorption spectrum of the *trans*-anethole radical cation generated by 308 nm photoionization in acetonitrile has absorption maxima at 380 and 600 nm, Figure 1, and is typical of the spectra observed for a variety of substituted styrenes. A similar spectrum is obtained using the 9,10-dicyanoanthracene (DCA)/biphenyl system in an oxygen-saturated solution to remove absorptions due to the 9,10-dicyanoanthracene radical anion. Chloranil sensitization also leads to the formation of the radical cation of *trans*-anethole, but in this case the absorption spectrum is complicated by the presence of a band at 450 nm due to the chloranil radical anion which cannot be removed by oxygen saturation.

The radical cation of *cis*-anethole is also readily generated by photoionization of *cis*-anethole in acetonitrile (Figure 1) or by photoinduced electron transfer using chloranil or 9,10-dicyanoanthracene/biphenyl. The radical cation has a strong absorption at 380 nm that is identical to that of the radical cation of *trans*-anethole, but the long wavelength band is slightly broader and is red-shifted by approximately 20 nm, Figure 1. This shift of the lowest energy absorption band is typical of spectra for a variety of *cis*- and *trans*-diarylalkenes.[9] The radical cations of 3-hydroxy-1-(4-methoxyphenyl)-1-propene and 3-methoxy-1-(4-methoxyphenyl)-1-propene (both trans) were also generated by 308-nm excitation of the parent alkene in acetonitrile. These radical cations have λ_{max} values of 385 and 610 nm (Figure 1) and are very similar to the *trans*-anethole radical cation.

The observed rate constant for the decay of the *trans*-anethole radical cation is ca. 4×10^4 s^{-1} in aerated acetonitrile and is independent of the concentration of anethole up to 0.10 M. This gives an estimate of $\leq 1 \times 10^6$ M^{-1} s^{-1} for the upper limit for the rate constant for addition of the radical cation to its precursor. This is inconsistent with a previous estimate, based on Stern−Volmer product quenching of adduct formation, of approximately 2×10^6 M^{-1} s^{-1} for the addition of the *trans*-anethole

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(28) Johnston, L. J.; Schepp, N. P. *Pure Appl. Chem.* **1995**, *67*, 71−78.

Figure 2. Relationship between the observed rate constant for the growth of the anethole radical cation at 600 nm and the concentration of 1,2-dianisyl-3,4-dimethylcyclobutane (**4**) in acetonitrile. Linear least-squares analysis of the data obtained at cyclobutane concentrations <0.002 M gives a slope = 2.2×10^{10} M^{-1} s^{-1}.

radical cation to neutral *trans*-anethole in acetonitrile.[29] The electron-transfer-sensitized cycloreversion of the anethole cyclobutane dimer was therefore examined in order to test whether rapid cleavage of the cyclobutane radical cation was responsible for the apparent insensitivity of the anethole radical cation decay to the precursor concentration.

Laser excitation of chloranil in the presence of the *all-trans*-1,2-dianisyl-3,4-dimethylcyclobutane (**4**, 0.0002−0.007 M) resulted in efficient quenching of the chloranil triplet, with the concomitant formation of both the chloranil radical anion (λ_{max} = 450 nm) and the anethole radical cation (λ_{max} = 600 and 380 nm). This confirms that the initial cyclobutane radical cation produced by electron transfer from the cyclobutane to triplet chloranil does indeed fragment rapidly to generate the anethole radical cation and, presumably, neutral anethole.[29] At low concentrations of cyclobutane (≤0.002 M) the observed rate constant for the formation of the anethole radical cation is the same as that for the decay of triplet chloranil, and a linear relationship is observed between the observed rate constant for the growth of the radical cation and the cyclobutane concentration, Figure 2. This leads to a rate constant for triplet quenching of 2.2×10^{10} M^{-1} s^{-1}. Under these conditions, electron transfer rather than cleavage of the cyclobutane radical cation is the rate-determining step for formation of the anethole radical cation. However, at higher concentrations of cyclobutane (above 0.002 M), the observed rate constant for formation of the anethole radical cation begins to level off and eventually reaches a plateau value of $\sim 8 \times 10^7$ s^{-1} at >0.005 M. This indicates that electron transfer is no longer the rate-determining step in the formation of the anethole radical cation.

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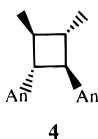
Previous estimates for the rate constants for the intramolecular cyclization of radical cations derived from **1**–**3** were based in part on the rate constant for reaction of **1**$^{\bullet+}$ with ethyl diazoacetate obtained by a competitive method, k_{EDA} = 1.5×10^6 M^{-1} s^{-1} in dichloromethane.[11] In the present work, direct measurement of the rate constants for the reaction of the *trans*-anethole and 3-methoxy-1-(4-methoxyphenyl)-1-propene radical cations with ethyl diazoacetate was accomplished by measuring the radical cation decay as a function of [EDA]. This led to rate constants of k_{EDA} = 1.3×10^7 and 1.4×10^7 M^{-1} s^{-1},

(29) Lewis, F. D.; Kojima, M. *J. Am. Chem. Soc.* **1988**, *110*, 8664−8670.
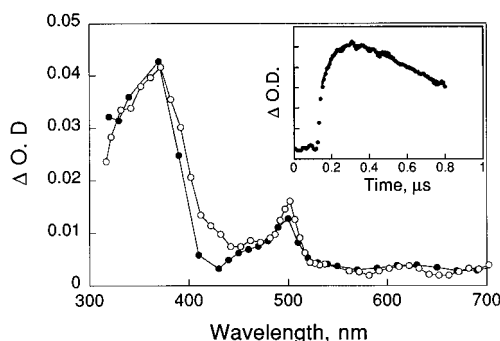
Figure 3. Transient absorption spectra measured immediately after direct 308-nm laser irradiation of probe **1** (○), and after 355-nm laser irradiation of 9,10-dicyanoanthracene in the presence of 0.08 M biphenyl and 0.001 M probe **1** (●) in oxygen-saturated acetonitrile. The inset shows the growth and the decay of the transient at 500 nm generated by direct 308-nm laser irradiation of **1**.

respectively, in acetonitrile at room temperature. A slightly higher rate constant of $\sim 3.5 \times 10^7$ M^{-1} s^{-1} was measured for the 3-methoxy-1-(4-methoxyphenyl)-1-propene radical cation in dichloromethane, although this experiment is considerably more difficult due to the low radical cation yield in this solvent. Thus, it appears that the rate constant for reaction of **1**$^{\bullet+}$ with EDA in dichloromethane is approximately 10 times larger than the previous estimate.

Nanosecond and Picosecond Flash Photolysis of 1. Laser irradiation of probe **1** in oxygen-saturated acetonitrile under the same conditions used to generate anethole radical cations gave a spectrum with absorption maxima at 500 and 370 nm, Figure 3. A similar spectrum is observed in nitrogen-saturated acetonitrile, except that in this case there is an additional band at 320 nm. In both cases, the transient spectra are quite clearly different from those observed for the radical cations of either anethole or 3-methoxy-1-(4-methoxyphenyl)-1-propene shown in Figure 1 and are inconsistent with a radical cation localized on one of the arylalkene moieties of **1**.[30,31] A detailed examination of the kinetic behavior at various wavelengths indicates that the 500 and 370 nm bands are not due to a single species, as outlined below.

The 500-nm transient is not produced within the laser pulse, but grows in with a rate constant of approximately 1.1×10^7 s^{-1}, and then decays more slowly in a first-order manner with a rate constant of 1.0×10^6 s^{-1}, Figure 3 (inset). Neither the growth nor decay of the 500-nm band is affected by oxygen, but the decay of the 500-nm band is accelerated in the presence of nucleophiles such as water, methanol and azide.[32] Measurement of the observed rate constants for the decay of the 500-nm band as a function of nucleophile concentration gave the following second-order rate constants for the reaction of the transient with nucleophiles: k_{water} = 4.6×10^7 M^{-1} s^{-1}, $k_{methanol}$ = 2.0×10^7 M^{-1} s^{-1}, and k_{azide} = 2×10^{10} M^{-1} s^{-1}.

(30) In some experiments, particularly for nitrogen-saturated samples, there is evidence of a weak and relatively short-lived absorption in the 600−650-nm region. This signal appears to result largely from product buildup or arylalkene-containing impurities in probe **1**. It may also reflect a minor amount of trapping of the solvated electron to give an arylalkene radical anion in the photoionization experiments. Note that in general the spectra for a particular arylalkene radical cation and anion are similar.[31]

(31) Shida, T. *Electronic Absorption Spectra of Radical Ions*; Elsevier: Amsterdam, 1988.

(32) The lifetime of the 500-nm transient showed some variation from one experiment to the next, most likely as a result of varying water content in the acetonitrile. On the basis of measured rate constant for reaction with water, even 0.02% water is sufficient to change the observed rate constant for decay by ~50%, and it is difficult with our experimental setup for flow experiments to adequately control the water content below this level. There is also some indication that the lifetime decreases slightly with increasing concentration of **1**.
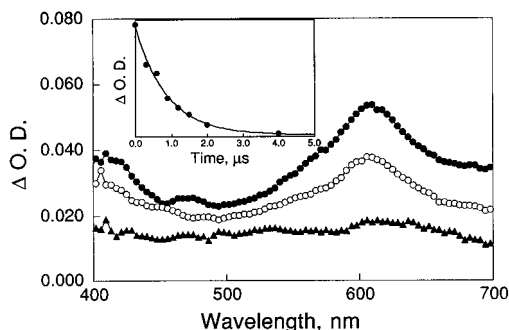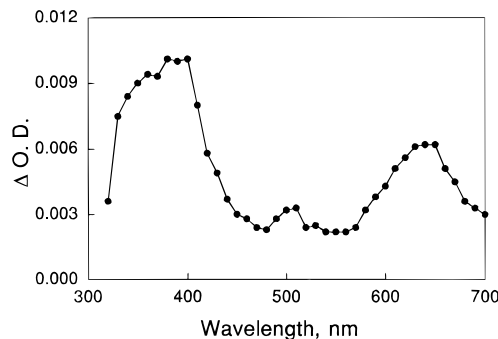
Figure 4. Transient absorption spectra generated upon 266-nm picosecond laser irradiation of probe **1** in acetonitrile. Spectra were recorded immediately (●), 1000 ps (○) and 5000 ps (▲) after the laser pulse. The inset shows the time-resolved decay at 600 nm.

Figure 5. Transient absorption spectrum measured immediately after 266-nm laser irradiation of probe **2** in oxygen-saturated acetonitrile.

By contrast to the 500-nm transient, the 370-nm absorption is produced promptly after the laser pulse. In oxygen-saturated acetonitrile, it decays with a rate constant of 3×10^5 s^{-1} that is significantly slower than those for both the formation and decay of the 500-nm band. A broad residual absorption between 310 and 380 nm remains after the initial first-order decay of the 370 nm band. In nitrogen-saturated acetonitrile, the decay of the 370-nm band is made up of a fast component and a slow component. The slow component decays with a rate constant that is similar to that observed in oxygen-saturated acetonitrile. The fast component decays with a rate constant of about 4×10^6 s^{-1} and, since it is not observed in oxygen-saturated acetonitrile, is likely due to either a triplet species or the radical anion of probe **1** produced by trapping of the electron generated in the initial photoionization. In nitrogen-saturated acetonitrile, an additional band at 320 nm is produced within the laser pulse and does not decay over the time scale of the experiment. In addition, a weak band at 380 nm remains after the decay of the 370-nm band is complete.

Quenching of the 370-nm band by nucleophiles was carried out in oxygen-saturated acetonitrile in order to remove the complicating features observed in nitrogen-saturated solution. This species is quenched by nucleophiles such as methanol and azide with rate constants of $k_{\mathrm{methanol}} = 2.2 \times 10^6$ M^{-1} s^{-1} and $k_{\mathrm{azide}} = 3 \times 10^{10}$ M^{-1} s^{-1}, respectively. The order of magnitude difference in the rate constants for methanol quenching of the 370- and 500-nm absorptions further confirms the presence of two distinct transients.

The radical cation of probe **1** was also produced by photoinduced electron transfer using DCA/biphenyl as sensitizer in oxygen-saturated acetonitrile. The biphenyl radical cation was quenched by **1** with a rate constant of 1.8×10^{10} M^{-1} s^{-1} to give a transient spectrum with absorption bands at 500 and 370 nm that is identical to that observed upon photoionization of **1**, Figure 3. The decay kinetics for the 500-nm transient were similar to those observed by direct excitation of **1**, although the growth occurred more rapidly under the sensitized conditions.

Picosecond laser irradiation of probe **1** gave quite different results from those described above for the nanosecond experiments. The absorption spectra generated by 266-nm, 35-ps irradiation of **1** in acetonitrile are shown in Figure 4. With the increased time resolution provided by the picosecond spectrometer, a strong absorption at 610 nm is observed immediately after the laser pulse and then decreases rapidly and is completely gone after 4 ns. The 610-nm absorption decayed with first-order kinetics with a rate constant of 1.2×10^9 s^{-1}, Figure 4, inset, which explains the fact that a similar absorption was not observed upon nanosecond irradiation. No absorption at 500 nm was observed at the longest delay used in the picosecond
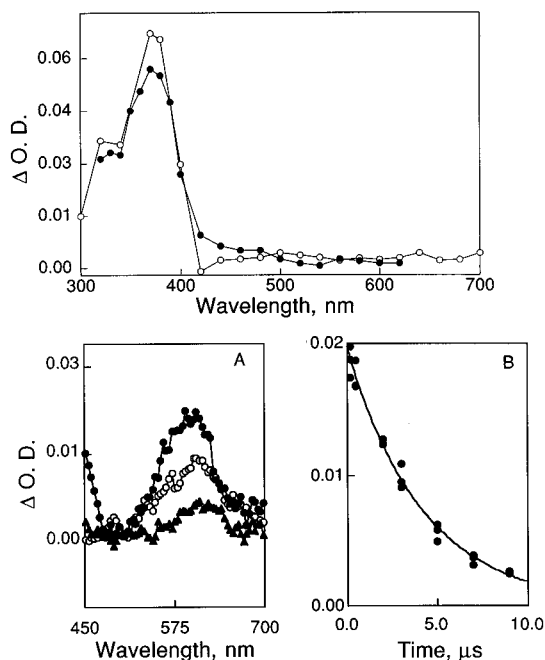
experiments ($\sim$8 ns), consistent with the growth rate constant of $\sim$1 $\times$ 10^7 s^{-1} measured for the 500-nm species in the nanosecond experiments.

Nanosecond and Picosecond Flash Photolysis of 2. Nanosecond 308-nm laser photolysis of **2** in oxygen-saturated acetonitrile gave the transient spectrum shown in Figure 5. There are strong absorptions at 640 nm and between 320 and 420 nm, as well as a weaker band at 500 nm. A similar spectrum is obtained by photoinduced electron transfer using the DCA/biphenyl cosensitizer method in oxygenated acetonitrile. The 640-nm absorption generated by direct irradiation of **2** decayed with a first-order rate constant of $\sim$3 $\times$ 10^6 s^{-1}, was unreactive toward oxygen and methanol (up to 1 M), and reacted with azide with a diffusion-controlled rate constant of $\sim$3 $\times$ 10^{10} M^{-1} s^{-1}. The 500-nm band decayed with a rate constant of 1.5×10^6 s^{-1} in both oxygen- and nitrogen-saturated acetonitrile. This transient did not appear to be formed instantaneously within the laser pulse, but its rapid decay and the small signal intensity made it impossible to determine a rate constant for its growth. In oxygen-saturated solution, the decay kinetics in the 300−400-nm region are complex. A fraction of the absorption in this region clearly decays on a time scale similar to that of the 640-nm signal; although the two components are difficult to separate kinetically, there is evidence for more rapid decay at 410 than at 360 nm, and there is also a longer-lived residual absorption (λ_{max} at $\sim$360 nm) that remains after both the 640- and 500-nm bands have completely decayed. The short-lived component is unaffected by methanol but does react with azide, with an approximate rate constant of 3×10^{10} M^{-1} s^{-1}.

The spectrum obtained by 308-nm irradiation of **2** in nitrogen-saturated acetonitrile differs somewhat from those obtained under oxygen at wavelengths below 450 nm. The absorption at 400 nm decays more slowly than in oxygen-saturated acetonitrile, and there are clearly absorption maxima at 400 and 340 nm that remain after the decay of the 640- and 500-nm transients. The combined results under oxygen and nitrogen suggest that the 640-nm transient has a second absorption band at approximately 360 nm. There is at least one additional species that is longer-lived under nitrogen, has λ_{max} at 400 and 340 nm, and reacts with oxygen to generate the residual signal at 360 nm that is detected after the decay of the 640-nm transient under oxygen.

Nanosecond and Picosecond Flash Photolysis of 3. Irradiation of probe **3** in oxygen- or nitrogen-saturated acetonitrile with the nanosecond 308-nm laser led to the formation of a transient species with absorption at 370 nm, Figure 6. No evidence for the presence of a species with absorption at 500 nm was observed, nor was there absorption at 600 nm as expected for an arylalkene radical cation. Similar results were obtained upon DCA/biphenyl-sensitized irradiation; only the band at 370 nm was observed, with no evidence for absorption

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Product Studies. Direct Irradiation of 1. Direct 300-nm irradiation of **1** in acetonitrile (0.0045 M, nitrogen-saturated) generated cyclobutane **5** which was identified by comparison with an authentic sample obtained by the triarylaminium salt-catalyzed cyclization of **1**. These results are consistent with the expected [2 + 2] intramolecular photocycloaddition of **1**. There was also a minor product (10%) which had a retention time and mass spectral data (*m/z* 310) consistent with its assignment to the isomeric *trans*-cyclobutane **6**, which has previously been observed as a product of benzophenone-sensitized irradiation of **1**.[24] At low conversions, an additional material which appeared to be an isomer of the starting material (**7**) on the basis of GC/MS data was observed. Examination of the product ratios as a function of time indicated that **5** and **7** were primary products, whereas a short induction period was required before the observation of **6**. The yield of **7** reached a maximum (~10% of mixture) at ~50% conversion but was barely detectable above 90% conversion, clearly indicating that **7** yields **5** or **6** under the reaction conditions. Although **7** was not produced in sufficient yield for isolation, ^{1}H NMR of an irradiated sample of **1** in acetonitrile showed a characteristic doublet of triplets at δ 5.38 ($J = 11$ Hz) in addition to the signals for **1** and **5**. This is consistent with the expected chemical shift and coupling constant for the β-vinylic H of the partially isomerized (cis) starting material (**7**), based on the spectra for related *cis*-styrenes. The characteristic doublet of triplets disappeared upon prolonged irradiation, in agreement with the GC results. These results indicate that cyclobutane **6** is formed via direct [2 + 2] photocycloaddition of **7** generated by photoinduced cis−trans isomerization of **1**. Similar results were obtained upon irradiation of **1** in methylene chloride in that both **5** and **7** were observed as primary products with delayed formation of **6**. Isomer **7** was more slowly converted to products in this case.

6   **7**
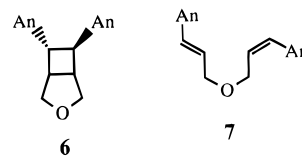
Chloranil Photosensitization of 1. Generation of **1**•+ by photoinduced electron transfer using triplet chloranil gave a number of additional products that were not observed previously when this radical cation was generated using a triarylaminium salt as the electron transfer catalyst.[11] For example, 350-nm (Rayonet) irradiation of a nitrogen-purged solution of 0.0014 M chloranil and 0.004 M **1** in acetonitrile resulted in the efficient consumption of **1**, and GC and GC/MS analysis indicated the formation of four products at high conversions. One of these products was identified as cyclobutane **5**, by comparison with an authentic sample. A second product was assigned to the isomeric cyclobutane **6**, detected as a minor product in the direct [2 + 2] photocycloaddition. Further irradiation of a solution containing all four products led to the complete consumption of **1** and the two cyclobutanes and resulted in the formation of increased amounts of the other two products (**8** and **9**, *m/z* 308 and 306, respectively). Prolonged irradiation of this mixture in the presence of additional chloranil resulted in the conversion of **8** to **9**. This material was isolated and identified as the
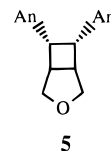

Figure 6. (Top) Transient absorption spectra generated upon 308-nm irradiation of probe **3** in air-saturated acetonitrile (●), and upon 355-nm-excitation of dicyanoanthracene with 0.08 M biphenyl and 0.001 M probe **2** in oxygen-saturated acetonitrile (○). (Bottom) Transient absorption spectra generated upon 266-nm picosecond laser irradiation of probe **3** in acetonitrile (A). Spectra were recorded 200 ps (●), 2000 ps (○) and 5000 ps (▲) after the laser pulse. Time-resolved decay at 600 nm (B).

at 600 or 500 nm, Figure 6. In oxygen-saturated acetonitrile, the 370-nm band decayed completely in a first-order manner with a rate constant of 5×10^5 s^{-1}. In nitrogen-saturated solution, the rate constant for the decay at 370 nm remained largely unchanged, but there was significant residual absorption, indicating the presence of a long-lived species in this region that is quenched by oxygen. While oxygen has no influence on the rate constant for the decay of the band at 370 nm, the rate constant does increase in the presence of quenchers such as methanol and azide with rate constants $k_{methanol} = 3.5 \times 10^7$ M^{-1} s^{-1} and $k_{azide} = 3 \times 10^{10}$ M^{-1} s^{-1}. These rate constants were measured in oxygen-saturated solution to eliminate the residual absorption at 370 nm observed in nitrogen-saturated acetonitrile.

While no 600-nm absorption was observed upon direct or sensitized excitation of **3** using the nanosecond system, picosecond irradiation of **3** in acetonitrile gave a spectrum with λ_{max} at ~600 nm (Figure 6) which is similar to that observed for probe **1**. This absorption decayed with first-order kinetics with a rate constant of 3.0×10^8 s^{-1} (Figure 6). Since the spectral window attainable with the picosecond spectrometer is limited to $\lambda > 410$ nm, it is not possible to determine whether the 370-nm transient observed in the nanosecond experiments is detectable at early times.

Nanosecond Flash Photolysis of Cyclobutane 5. The generation of the radical cation from cyclobutane **5** was attempted using DCA/biphenyl. The biphenyl radical cation was quenched by **5** to give a transient absorption spectrum with λ_{max} at 500 nm that was similar to that observed from probe **1**. There was no evidence for an arylalkene radical cation in the 600-nm region although there was an additional transient at ~430 nm. The 500-nm transient decayed with a rate constant of ~3×10^6 s^{-1}, which is somewhat larger than typically observed for the 500-nm transient from **1**, although some variation in lifetime has been observed in the latter case.[32]

substituted naphthalene, **9**. Compound **8** could not be readily separated from **9**; however, it was assigned to dihydronaphthalene **8**, based on its facile conversion to **9**, GC/MS data, and the presence of a characteristic olefinic proton at 6.7 ppm in the NMR of a mixture of **6**, **8**, and **9**. This is further supported by the fact that substituted dihydronaphthalenes are produced as products of the radical cation-initiated dimerization of a variety of substituted styrenes and diarylalkenes.[21,27,33-38]

8   **9**
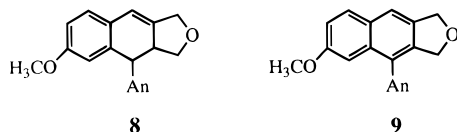
The products obtained from the chloranil (0.0014 M)-sensitized irradiation of **1** in acetonitrile were examined at several different concentrations of **1**. A xenon lamp with a 375-nm cutoff filter was used for these experiments to eliminate any possibility of products arising from the direct photocycloaddition of **1**. Furthermore, the product ratios were measured at low conversions (≤5%) in order to minimize the amount of photosensitized decomposition of the products. At 0.04 M **1**, cyclobutane **5** was the major product, accounting for 97% of the product mixture at 2% conversion with the remaining 3% being dihydronaphthalene **8**. At 11% conversion, cyclobutane **6** was also observed with the product ratio being 65:22:13 for **5**:**8**:**6**. For 0.004 M **1**, the same three products were observed in a ratio of 36:63:1 at 4% conversion. The relative amount of cyclobutane **6** increased substantially with conversion, although the ratio of **5**:**8** did not change dramatically.

Chloranil-Sensitized Irradiation of 5. Irradiation (350 nm, Rayonet) of a solution containing 0.001 M chloranil and 0.03 M **5** resulted in the formation of **8** as the major product with a smaller amount of **9**. At low conversions (≤10%) only **8** was observed, and there was no evidence for the formation of either the isomeric cyclobutane **6** or **1** (or its isomer **7**).

Tris(4-bromophenyl)aminium Hexachloroantimonate-Catalyzed Cyclization of 1. Cyclization of **1** using the tris-(4-bromophenyl)aminium salt as an electron transfer catalyst with reaction conditions as reported previously[11] gave cyclobutane **5** as the sole product. However, doubling the reaction time resulted in the observation of a small amount of the dihydronaphthalene product (**8**, ~7%). Addition of aminium salt to the mixture of **5** and **8** isolated from this reaction resulted in the complete disappearance of **5** and the formation of a mixture of **6**, **8**, and **7**. A 10-fold reduction in the concentration of both **1** and the catalyst and a reaction time of 15 s resulted in the formation of complex mixtures containing both cyclobutanes **5** and **6**, as well as **8** and **7**.

Discussion

Anethole Dimerization. The spectra obtained for the *cis*- and *trans*-anethole and 3-methoxy-1-(4-methoxyphenyl)-1-propene radical cations indicate that replacement of one of the β-methyl hydrogens with a methoxy group has relatively little effect on the absorption properties of the radical cations. This demonstrates that the latter provide good models for the radical

Scheme 2
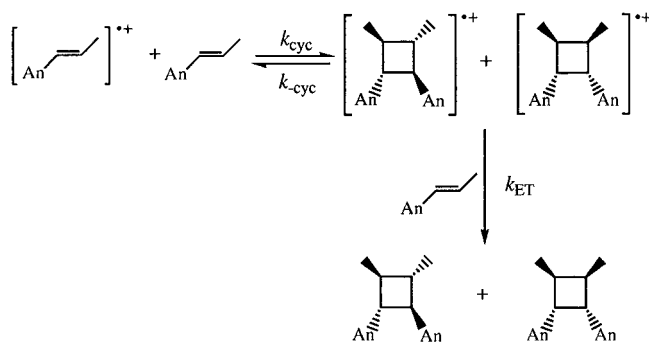
cations of the three intramolecular probes, at least in terms of their spectral characteristics. The apparent insensitivity of the decay of the *trans*-anethole radical cation to the precursor concentration is at first glance at odds with results of previous product studies by Lewis and Bauld.[29,39] These have shown that *trans*-anethole dimerizes efficiently under photoinduced electron transfer conditions to give a mixture of the syn and anti head-to-head cyclobutane dimers that retain the original trans stereochemistry of the starting alkene. Stern−Volmer product quenching studies led to an estimate of approximately 2×10^6 M^{-1} s^{-1} for the cycloaddition of the *trans*-anethole radical cation to neutral *trans*-anethole in acetonitrile, k_{cyc}, Scheme 2.[29] The discrepancy between this estimate and the present results may result either from fragmentation of the initial cyclobutane radical cation or from its reduction to the neutral 1,2-dianisyl-3,4-dimethylcyclobutane by excess anethole present in solution, k_{-cyc} and k_{ET}, respectively, in Scheme 2. Both of these reactions will regenerate the anethole radical cation and result in a constant rate constant for its decay, as long as k_{cyc} is slower than either k_{-cyc} or k_{ET}.

Both previous product studies[29,40] and our transient experiments indicate that the cyclobutane products undergo cycloreversion to yield *trans*-anethole under photosensitized electron transfer conditions. The results obtained upon generation of **4**[•+] using choranil as a sensitizer indicate that at low concentrations of **4** the formation of the anethole radical cation reflects the initial electron transfer rate. At high concentrations of **4**, electron transfer is no longer rate limiting and the observed rate constant for growth of the anethole radical cation of ~8×10^7 s^{-1} represents the cleavage rate constant, k_{-cyc}. The short lifetime of the cyclobutane radical cation due to its rapid cycloreversion thus explains the lack of dependence of the anethole radical cation decay on the concentration of neutral anethole.

Intramolecular Cyclization of Probe 1. Picosecond laser irradiation of probe **1** in acetonitrile under conditions that result in photoionization of a variety of arylalkenes generates a short-lived transient with an absorption maximum at 600 nm. This transient is almost identical to those observed on a nanosecond time scale for *trans*-anethole and 3-methoxy-1-(4-methoxyphenyl)-1-propene and is assigned to a radical cation (**1**[•+]) localized on one of the arylalkene moieties. The short lifetime for **1**[•+] precludes its detection in a nanosecond experiment. However, under these conditions the formation of a 500-nm transient that reacts with nucleophiles but not with oxygen is observed. This result is reminiscent of our earlier studies on the radical cation dimerization of 4-methoxystyrene.[27] In this case, addition of the radical cation to the parent alkene generates an initial cyclobutane radical cation that rearranges to a hexatriene radical

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(34) Asanuma, T.; Yamamoto, M.; Nishijima, Y. *J. Chem. Soc., Chem. Commun.* **1975**, 608−609.
(35) Kadota, S.; Tsubono, K.; Makino, K.; Takeshita, M.; Kikuchi, T. *Tetrahedron Lett.* **1987**, *28*, 2857−2860.
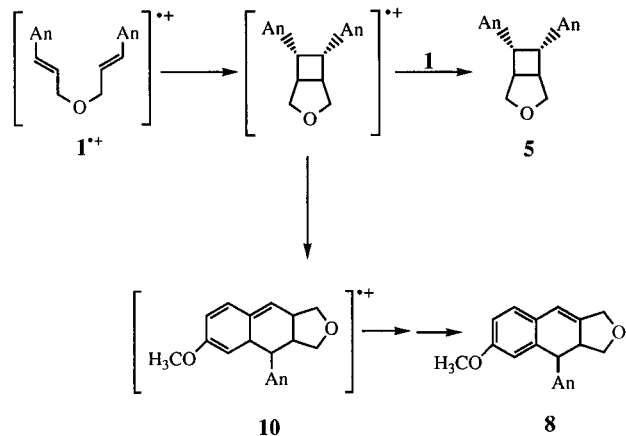(36) Kojima, M.; Sakuragi, H.; Tokumaru, K. *Bull. Chem. Soc. Jpn.* **1989**, *62*, 3863−3868.
(37) Mattes, S. L.; Farid, S. *J. Am. Chem. Soc.* **1983**, *105*, 1386−1387.
(38) Mattes, S. L.; Farid, S. *J. Am. Chem. Soc.* **1986**, *108*, 7356−7361.

(39) Bauld, N. L.; Pabon, R. *J. Am. Chem. Soc.* **1983**, *105*, 633−634.
(40) Pac, C.; Fukunaga, T.; Go-An, Y.; Sakae, T.; Yanagida, S. *J. Photochem. Photobiol., A* **1987**, *41*, 37−51.

Scheme 3

cation that absorbs at 500 nm and is the precursor to the observed dihydronaphthalene product. The observation of a similar 500-nm transient from **1** and the fact that both cyclobutane and dihydronaphthalene products are observed in the radical cation-initiated cyclization of **1** suggests a similar mechanism, as summarized in Scheme 3. Initial cyclization of **1**[•+] generates a cyclobutane radical cation that is either reduced to cyclobutane **5** or rearranges to a hexatriene radical cation (**10**) that absorbs at 500 nm and leads to product **8**. There is ample precedent for such a rearrrangement since radical cations of a number of vinylcyclobutanes (including those derived from *trans*-anethole radical cation cycloadditions) undergo 1,3-shifts to give 6-membered ring products.[19] The observation of rearranged dihydronaphthalene products is common in arylalkene dimerization and has frequently been attributed to the intermediacy of a 1,4-acyclic radical cation.[33−38] However, the present results and literature precedent for both *trans*-anethole and 4-methoxystyrene provide convincing evidence for a cyclobutane radical cation as the primary intermediate.[27,29,39]

The measured rate constant of 1.2×10^9 s^{-1} for decay of the initial arylalkene radical cation provides an accurate measure for its rate of cyclization since there is no evidence for fragmentation of the cyclobutane radical cation. This is based on the fact that independent generation of the cyclobutane radical cation (**5**[•+]) by photosensitized electron transfer does not produce a transient absorption due to **1**[•+], nor do product studies under these conditions show any formation of **1**. The transient results obtained by photosensitized electron transfer generation of **5**[•+] are also consistent with Scheme 3 in that the same 500-nm transient generated from **1** is obtained.

The variation in product ratios as a function of the concentration of **1** is readily explained on the basis of Scheme 3. Cyclobutane **5** is the main product at high [**1**] (0.04 M) where reduction of **5**[•+] by excess **1** is the dominant reaction. By contrast, at lower [**1**] (0.004 M) dihydronaphthalene **8** is the major product, since reduction of **5**[•+] no longer competes efficiently with rearrangement to the hexatriene radical cation. The product ratios must be measured at low conversion as photosensitized electron transfer chemistry of the cyclobutane leads to dihydronaphthalene **8**. Electron transfer quenching of triplet chloranil is sufficiently exergonic to occur at a diffusion-controlled rate for both **1** and **5**, for which oxidation peak potentials of 1.16 and 1.23 V (vs SCE in acetonitrile) have been measured.[41,42] The original triarylaminium salt-catalyzed cyclization of **1** was carried out at high concentrations of **1**, thus

preventing the rearrangement of the cyclobutane radical cation.[11] Since the triarylaminium salt has a relatively low oxidation potential (0.85 V vs SCE),[19] electron transfer will be endothermic for both **1** and **5**; cyclobutane **5** is ~0.1 V more difficult to oxidize than **1**, thus favoring the generation of **1**[•+] rather than **5**[•+] in the trarylaminium salt-catalyzed reaction. As a result the radical cation-initiated chemistry of the cyclobutane does not pose a problem at high concentrations of **1** and short reaction times, and it is straightforward to obtain good yields of **5** using the triarylaminium salt catalyst. By contrast, the more energetic triplet chloranil system produces a mixture of products under similar conditions. The triarylaminium salt-catalyzed reaction also gives complex mixtures at longer reaction times and lower concentrations of **1**.

The measured rate of growth of the 500-nm transient formed by photoionization of **1** provides an estimate of ~100 ns for the lifetime of the cyclobutane radical cation. Note that the low concentration of **1** (~0.3 mM) used in this experiment minimizes any competing reduction of **5**[•+] so that the measured rate constant reflects predominately rearrangement. By contrast, the photosensitized experiments using dicyanonaphthalene/biphenyl are done at higher concentrations of **1** (~5 mM) and result in a substantially faster growth for the 500-nm signal.

As noted above, the product studies using chloranil are complicated by the interconversion of **5** and **8**, leading to product ratios that vary with irradiation time. Substantial yields of cyclobutane **6** are also observed at higher conversions; the isomerized cyclobutane clearly does not result from the photosensitized formation of **5**[•+] since control experiments indicate that this leads only to **8**. A plausible route for formation of **6** is back electron transfer to generate triplet **1** which can then undergo cis−trans isomerization to **7**, followed by radical cation-initiated cyclization to **6**. Cis−trans isomerization of starting material has been observed in the photoinduced electron transfer chemistry of *cis*- and *trans*-anethole so there is clearly precedent for such a reaction.[29] Furthermore, the formation of **6** via intermediate generation of **7** has also clearly been observed in the direct photocycloaddition and under benzophenone-sensitized conditions.[24] The variation in the yields of dihydronaphthalene **8** and the cyclobutane products at low concentration of **1** may indicate that back electron transfer to generate triplet **1** can also lead to direct [2 + 2] photocycloaddition.

The rapid cyclization of **1**[•+] is in reasonable agreement with the previous estimate, particularly given the difference in solvent and conditions used in the two experiments.[11] Intramolecular cyclization occurs more rapidly than the related intermolecular addition of anethole radical cation to the parent alkene, for which a bimolecular rate constant of ~2×10^6 M^{-1} s^{-1} has been estimated.[29] The fate of the cyclobutane radical cation is also different: **5**[•+] has a lifetime of ~100 ns that is limited by rearrangement in the absence of high concentrations of reducing agent, while **4**[•+] has a lifetime of ~10 ns that is limited by cleavage to regenerate anethole and its radical cation. Our present estimate for the lifetime of this cyclobutane radical cation is considerably shorter than that reported in an earlier product study.[40] The radical cation of the cyclobutane formed by dimerization of 4-methoxystyrene is also short-lived (3 ns) and decays by a combination of cleavage and rearrangement to a hexatriene radical cation.[27]

The intramolecular cyclization rate constant of 1.2×10^9 s^{-1} measured for **1**[•+] can also be compared to literature results for related intramolecular reactions of 1,ω-bis(diarylethenyl)alkane radical cations.[43,44] For example, the radical cation of 1,1,7,7-

(41) Triplet chloranil will oxidize donors with E_{ox} <2.25 V at a diffusion controlled rate.[42]

(42) Wayner, D. D. M. In *Handbook of Photochemistry,* Scaiano, J. C., Ed.; CRC Press: Boca Raton, 1989; Vol. 2, Chapter 18.

(43) Tamai, T.; Mizuno, K.; Hashida, I.; Otsujo, Y.; Ishida, A.; Takamuku, S. *Chem. Lett.* **1994**, 149−152.

tetrakis(4-methoxyphenyl)-1,6-heptadiene decays with a rate constant of 1×10^8 s^{-1} to give a transient assigned to the 1,4-acyclic radical cation.[43] The cyclization rate constant is approximately 2 orders of magnitude slower than estimates for the related intermolecular dimerization of 1,1-bis(4-methoxyphenyl)ethene.[38] Estimates for the cyclization of 1,1,ω,ω-tetrakis(4-methoxyphenyl)-1,7-octadiene and -1,5-hexadiene radical cations of $\sim10^8$ and 3.6×10^6 s^{-1}, respectively, have also been reported.[43]

Intramolecular Cyclization of Probes 2 and 3. Direct irradiation of probes **2** and **3** also gives transients in the 600-nm region that are consistent with the formation of radical cations localized on an arylalkene moiety. In the case of **3**, the radical cation is short-lived and can be detected only in a picosecond experiment. For **2**, the initial transient has an absorption that is slightly red-shifted from that observed for **1** and **3**, consistent with the cis configuration of the two arylalkene groups and the fact that the *cis*-anethole radical cation has an absorption maximum at longer wavelength than the trans radical cation. There is also a shorter wavelength absorption in the 380-nm region that is typical of arylalkene radical cations.[9] The radical cation assignment for the initial transient obtained from **2** is supported by its high reactivity toward azide, its insensitivity toward methanol and oxygen, and its generation by photosensitized electron transfer. Note that the reaction of the anethole radical cation with methanol occurs too slowly to measure using nanosecond techniques and that most substituted styrene radical cations are unreactive toward oxygen.[26]

The transient results for probe **2** indicate that the initial arylalkene radical cation is much longer lived than that from probe **1**, despite the fact that both undergo intramolecular dimerization. The presence of a 500-nm transient suggests that rearrangement to a hexatriene radical cation occurs in this system as well. The apparent slow cyclization is in contrast to the original estimate of $\geq3 \times 10^9$ s^{-1} based on product studies.[11] It is possible that the rigid structure of probe **2** prevents the radical cation and the neutral alkene from achieving the optimum orientation for adduct formation, resulting in relatively slow cyclization. However, an alternate explanation is that cyclization of **2**$^{\bullet+}$ is faster than 3×10^6 s^{-1} but that fragmentation of the adduct radical cation occurs even more rapidly, as observed for the radical cation of cyclobutane **4**. If this is the case, the measured decay of the 640-nm transient reflects gradual loss of a mixture of cyclobutane and arylalkene radical cations via some other reaction, presumably rearrangement to give the 500-nm transient. More detailed transient and product studies would obviously be required to establish whether rearrangement products are observed and to obtain a reliable cyclization rate for **2**$^{\bullet+}$.

The transient results for probe **3** are less complicated than those for **1** and **2**, and there is no evidence for rearrangement of the initial adduct radical cation. The measured rate constant for decay of the arylalkene radical cation at 640 nm of 3.0×10^8 s^{-1} indicates that intramolecular cyclization is again considerably faster than related intermolecular reactions. For example, rate constants of 5.9×10^5 and 5.6×10^6 M^{-1} s^{-1} have been measured for the cycloaddition reaction between the anethole radical cation and 2,4-hexadiene and 1,3-cyclohexadiene, respectively.[45,46] The measured cyclization rate constant for **3**$^{\bullet+}$ is also approximately 1 order of magnitude faster than

previously estimated from the triarylaminium salt-catalyzed reaction.[11] This estimate was based on Stern–Volmer quenching of the formation of the Diels–Alder adduct with trimethoxybenzene, assuming a rate constant of 1.8×10^{10} M^{-1} s^{-1} for trapping of **3**$^{\bullet+}$ by trimethoxybenzene. The calculated cyclization rate for **3**$^{\bullet+}$ was combined with the product ratio for Diels–Alder adduct to cyclopropane obtained by generating **3**$^{\bullet+}$ in the presence of ethyl diazoacetate to give an estimate of 1.5×10^6 M^{-1} s^{-1} for the rate constant for trapping of **1**$^{\bullet+}$ with ethyl diazoacetate to give a cyclopropane product. However, our measured rate constants for the reactions of several related radical cations with ethyl diazoacetate are approximately 10 times larger than this estimate. The measured rate constant for ethyl diazoacetate, in combination with the cyclization/cyclopropanation product ratio from the previous work, leads to a revised estimate for the cyclization rate constant for **3**$^{\bullet+}$ of 3.3×10^8 s^{-1}. The agreement between the two methods after correction of one of the calibration rate constants used for the product study suggests that the cyclization rate constant of $\sim3 \times 10^8$ s^{-1} for **3**$^{\bullet+}$ is reliable. The absence of rearrangement for **3** also makes this an attractive choice of probe.

Both direct and photosensitized irradiations of probes **1–3** yield several different transients in the 330–400-nm region. Triplet excited states[47] and radical anions[31] of arylalkenes absorb in this region and react with oxygen and may thus account for the oxygen-sensitive transients. There is also a transient with λ_{max} in the 360–370-nm region that reacts with nucleophiles but not oxygen. Neither the absorption properties nor the relatively long lifetimes are consistent with literature data for the 4-methoxyphenethyl cation ($\lambda_{max} = 340$ nm),[48] so it is unlikely that the transients are arylmethyl carbocations derived from the probe molecules. For probes **1** and **2**, the observed transients may be related to further chemistry of the relatively short-lived hexatriene radical cation. In the case of probe **3**, cyclization will give an initial adduct radical cation that is the precursor to the final Diels–Alder product. The observed reactivity of the 370-nm transient toward nucleophiles is consistent with its assignment to the initial adduct radical cation, although the limited data available indicate that radical cations of simple alkenes usually have shorter wavelength absorptions.[9]

Conclusions

The radical cations of probes **1–3** can be generated by either photoionization or photoinduced electron transfer and have properties that are similar to those of anethole and related arylalkenes. The transient results indicate that **1**$^{\bullet+}$ cyclizes with a rate constant of 1.2×10^9 s^{-1} to give a cyclobutane radical cation with a lifetime of ~100 ns. The latter can either rearrange to a hexatriene radical cation that is the precursor to the observed dihydronaphthalene product or be reduced (by excess **1** at high concentrations) to cyclobutane **5**. There is no evidence for cleavage of the initial cyclobutane radical cation. The product studies under photosensitized electron transfer conditions are complicated by the conversion of **5** to dihydronaphthalene **8** and by the formation of trans isomers of both the probe and the cyclobutane product. The transient results suggest that **2**$^{\bullet+}$ cyclizes more slowly than does **1**$^{\bullet+}$, although the measured rate constant may reflect reversibility in the formation of the initial cyclobutane radical cation. The transient evidence in this case is also consistent with rearrangement to form a hexatriene radical cation. Given the fact that the estimates for cyclization of **2**$^{\bullet+}$ obtained by two different methods vary by almost 3 orders of

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(45) Schepp, N. P.; Johnston, L. J. *J. Am. Chem. Soc.* **1994**, *116*, 10330–10331.
(46) Schepp, N. P.; Johnston, L. J. *J. Am. Chem. Soc.* **1996**, *118*, 2872–2881.
(47) Bonneau, R.; Herran, B. *Laser Chem.* **1984**, *4*, 151–170.
(48) McClelland, R. A.; Kanagasabapathy, V. M.; Steenken, S. *J. Am. Chem. Soc.* **1988**, *110*, 6913–6914.

magnitude, it would be premature to conclude much for this system. It is likely that the chemistry of the initial radical cation adduct from **2** is complicated by competing fragmentation, rearrangement, and reduction to give the observed cyclobutane product, which is a limitation to its use as an intramolecular probe. By contrast, the radical cation of probe **3** undergoes intramolecular Diels−Alder cyclization with a rate constant of 3.0×10^8 s^{-1}, with no evidence for rearrangement.

The results for the three intramolecular probes based on radical cation cycloaddition reactions indicate that the use of these systems may be less straightforward than originally suggested. For example, **1**$^{\bullet+}$ can lead to two different products, depending on the concentration of **1** and the conditions used to generate the radical cation. In fact, the use of **1** as a probe at relatively low concentrations or under conditions where it is complexed, for example to an enzyme, will give a different product mixture than is obtained using typical electron transfer conditions. However, **1** is still a reasonably good choice for a radical cation probe given its rapid cyclization rate constant and, perhaps more importantly, the fact that the initial cyclobutane radical cation does not revert to starting material. Intramolecular Diels−Alder probe **3** has less complex chemistry, and its radical cation cyclizes approximately 1 order of magnitude more slowly than **1**$^{\bullet+}$. Thus **1** and **3** can be used to cover a modest range of time scales. The development of intramolecular radical cation probes based on cycloaddition chemistry clearly requires careful kinetic and mechanistic studies under a variety of conditions to provide a properly calibrated system. These should mimic as closely as possible the conditions under which the probe molecule will be used to test for the involvement of radical cations in a particular reaction. For arylalkene probes, the use of Diels−Alder cycloadditions may be a better choice than cyclobutanation reactions since the latter are frequently reversible and generate primary products that are often unstable to the reactions conditions.

Experimental Section

Materials and General Techniques. Chloranil was recrystallized from acetonitrile before use. *trans*-Anethole was purified by chromatography and *cis*-anethole was prepared by photosensitized isomerization of the trans isomer according to a literature method.[49] 9,10-Dicyanoanthracene and biphenyl were used as received. Acetonitrile was either used as received or dried by distillation over calcium hydride before use. The radical cation probes (**1−3**) and cyclobutane **5** were prepared as described previously,[11] and the purity was checked by GC and GC/MS prior to laser experiments. GC analysis was carried out with a Hewlett-Packard 5890 gas chromatograph (cross-linked methylsilicone column). GC/MS was performed using a Hewlett-Packard 5970 Series mass selective detector. Proton and carbon NMR were recorded on a Bruker AMX 500 spectrometer, and chemical shifts are reported in ppm relative to tetramethylsilane.

Preparation of 4-Methoxycinnamyl Methyl Ether. To a stirred solution of 1.0 g (6.1 mmol) of 4-methoxycinnamyl alcohol and 3.0 g (21.1 mmol) of methyl iodide in 10 mL of dichloromethane were added 100 mg (0.36 mmol) of tetra-*n*-butylammonium chloride and 5.0 mL of 40% aqueous sodium hydroxide. The reaction mixture was stirred for 4 h at room temperature and was then poured into 20 mL of water. The product was separated from the aqueous phase by extraction with diethyl ether and the aid of brine solution. The combined ether extract was washed with water (2×20 mL) and dried over anhydrous magnesium sulfate, and the ether was removed *in vacuo* to afford the crude product. Purification by flash silica gel chromatography with 6:1 hexanes/ethyl acetate as eluent afforded 0.48 g (52%) of pure ether as a colorless oil. ^{1}H NMR (CDCl$_3$) δ 7.32 (d, $J = 8.7$ Hz, 2H), 6.85 (d, $J = 8.7$ Hz, 2H), 6.57 (d, $J = 15$ Hz, 1H), 6.14 (dt, $J = 15.5$ Hz,

1H), 4.06 (dd, $J = 6.0$ Hz, 2H), 3.79 (s, 3H), 3.37 (s, 3H); ^{13}C NMR (CDCl$_3$) δ 159.06, 132.51, 129.37, 127.50, 123.50, 114.06, 73.43, 57.81, 55.03; GC/MS *m/z* 178, 147 (base), 135, 115, 103, 91, M$^+$ 178 calcd for C$_{11}$H$_{14}$O$_2$.

Steady State Photolysis of 1 in CH$_3$CN at 300 nm. A nitrogen-purged acetonitrile solution of **1** (0.0045 M) was irradiated through Pyrex at 300 nm (Rayonet RPR reactor equipped with 300 nm lamps) for 15−30 min. The solvent was then removed under reduced pressure, and the photoproducts were identified by GC and GC/MS comparisons with the authentic materials prepared separately. Conversions to photoproducts were determined by quantitative GC using 4-methoxycinnamyl alcohol as internal standard. GC and GC/MS analyses of the photolysate revealed the formation of **5** (90%, GC retention time = 19.50, MS M$^+$ 310, 240, 202, 148, 135, 91) as the major product. There was also a small amount (∼10%) of an additional product which was assigned to **6** (GC retention time = 20.45, MS M$^+$ 310, 240, 202, 148, 135, 91) based on retention time and the similarity of its GC/MS fragmentation pattern to that of **5**. Attempts to isolate **6** were unsuccessful because of its low yield and poor separation on a silica column.

The time-dependent photolysis of **1** was also examined. An acetonitrile solution of **1** (0.0045 M) in a Pyrex tube was irradiated at 300 nm, and aliquots were removed at regular intervals. GC and GC/MS analyses of the photolysate at short irradiation times revealed the formation of **5** along with a small amount of a new product **7** with *m/z* = 310; **6** was not observed at these short (ca. 1 min) irradiation times. Longer irradiation times showed the presence of **5−7**. On further irradiation, **7** was consumed and **5** and **6** were the only observable photoproducts. To establish the identity of **7**, a CD$_3$CN (1.0 mL) solution of **1** (0.007 M) in an NMR tube was irradiated at 300 nm for 10 min and examined by ^{1}H NMR. The ^{1}H NMR spectrum of the reaction mixture, in addition to the characteristic peaks due to **1** and **5**, showed a diagnostic doublet of triplets at δ 5.38 ($J = 11$ Hz) which was assigned to the β vinyl proton of **7**. The assignment is supported by the similar chemical shift and coupling constant for related *cis*-β-methylstyrenes (δ 5.5 and $J \simeq 10-10.5$ Hz). Further irradiation of the reaction mixture led to the disappearance of the doublet of triplets assigned to **7** and showed only the characteristic peaks due to **5**.

Chloranil-Sensitized Irradiation of 1 in CH$_3$CN. (a) Identification of 8 and 9. A nitrogen-purged CH$_3$CN (50 mL) solution of chloranil (0.0014 M) and **1** (0.0014 M) in a Pyrex tube was irradiated with 350-nm Rayonet lamps. At shorter irradiation times GC and GC/MS analysis revealed the formation of **5** as well as two other products (**8** and **9**). After 2 h, **9** was the major product along with a small amount of **8**. Since attempted separation of **9** and **8** on a silica gel column was unsuccessful, the mixture was subjected to further irradiation (at 350 nm) in the presence of added chloranil (ca. 0.003 M) to give **9** as the only product. The crude material was purified by preparative tlc (silica gel; 5:1 hexanes/ethyl acetate) to afford pure **9**. ^{1}H NMR (CDCl$_3$) δ 3.88 (s, 3H, OCH$_3$), 3.72 (s, 3H, OCH$_3$), 4.98 (s, 2H, ArCH$_2$), 5.24 (s, 2H, ArCH$_2$), 7.01 (d, 3H, $J = 8.3$ Hz, ArH), 7.27 (d, $J = 8.5$ Hz, ArH), 7.11 (dd, 1H, $J = 8.5$ Hz, ArH), 7.58 (s, 1H), 7.73 (d, 1H, $J = 8.5$ Hz); ^{13}C NMR (CDCl$_3$) δ 130.86, 130.50, 129.46, 129.23, 118.40, 117.95, 114.16, 114.03, 105.21, 104.54, 73.41, 73.09, 55.38, 55.32. GC/MS *m/z* 306, 277, 245, 202, 189, 138, 163, 131, 101, M$^+$ 306 calcd for C$_{20}$H$_{18}$O$_3$. Dihydronaphthalene **8** was identified on the basis of GC/MS data and the presence of a characteristic singlet at δ 6.71 for the olefinic proton in the ^{1}H NMR of a mixture of **5**, **8**, and **9**: ^{1}H NMR (CDCl$_3$) δ 2.33 (m, 1H), 2.68 (m, 2H), 3.76 (s, 2H), 3.71 (s, 3H), 3.87 (s, 3H), 4.03 (t, 1H), 6.71 (s, 1H), 7.01 (d, 1H), 7.03 (d, 2H), 7.15 (dd, 1H), 7.27 (d, 2H), 7.73 (d, 1H). This NMR data is in good agreement with that for a related dihydronaphthalene generated by radical cation-mediated dimerization of 4-methoxystyrene which has the equivalent olefinic proton at 6.5.[27]

(b) Time- and Concentration-Dependent Photolyses. Product ratios for the chloranil sensitized irradiation of **1** were measured by quantitative GC using 4-methoxycinnamyl alcohol as an internal standard. Samples of chloranil (0.0014 M) and **1** (0.0014−0.004 M) in nitrogen-purged CH$_3$CN were irradiated with a 75-W xenon lamp equipped with a water filter and a 370-nm cutoff filter. The progress of the reaction was followed by GC and GC/MS as a function of time, and product ratios are described in the Results section.

(49) Futamura, S.; Ohta, H.; Kamiya, Y. *Bull. Chem. Soc. Jpn.* **1982**, *55*, 2190−2194.

Laser Flash Photolysis. The nanosecond and picosecond laser flash photolysis systems have been described.[27,50] The samples were contained in 7×7 mm^2 quartz cells and were deaerated by nitrogen- or oxygen-purging as required. Flow cells connected to a sample reservoir with Teflon tubing were used for obtaining transient absorption spectra. Either a Lumonics HY750 Nd:YAG laser (10 ns/pulse; 266

nm, $\leq$60 mJ/pulse; 355 nm, $\leq$40 mJ/pulse) or EX530 excimer laser (308 nm; $\leq$40 mJ/pulse, 8 ns/pulse) was used for sample excitation for the nanosecond experiments. A continuum YG-601C Nd:YAG laser (35 ps/pulse) was used to generate the probe continuum beam (1064 nm; 15 mJ/pulse; 25 cm D$_2$O with 15% P$_2$O$_5$) and the sample excitation beam (266 nm, 6 mJ/pulse) for the picosecond experiments.

(50) Kazanis, S.; Azarani, A.; Johnston, L. J. *J. Phys. Chem.* **1991**, *95*, 4430−4435.